

Gheorghe Asachi Technical University of Iasi
Faculty of Chemical Engineering and Environmental Protection

**Innovative electroluminescent nanocomposites for a new
approach in polymer based light emitting devices**

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Scientific report

In this research stage, activities were directed both towards achieving composite electroluminescent and deepening of notable results obtained at the beginning of the stage. Besides the previously investigated CdSe Quantum Dots obtained in the previous stages, carbon nanostructures - Carbon Dots (C-Dots) with remarkable photoluminescence properties were extensively investigated. The experimental study led to a new synthesis method of C-Dots with the highest PLQY (80%) reported up to date. The prepared C-Dots present remarkable photoluminescence with blue to green shifting emission and absolute quantum yields varying from up to 80%, depending on the excitation wavelength and selected dispersion mediums. Interestingly, up-conversion from NIR to visible range was instrumentally recorded, the process being even visually observable. Further, the composition and morphology of the prepared C-Dots were studied using XPS, FT-IR, Raman, P-XRD, DLS and AFM investigation methods. Carbon Dots are a new class of carbon based nanostructured materials which start to gather much research interest due their remarkable properties such as tunable photoluminescence (PL) with high quantum yields (PLQY), lack of toxicity, chemical inertness, resistance to photobleaching etc. Although their photoluminescence is counted as one of the most interesting features considering the wide applications potential, the exact PL mechanism is still an open debate subject. In a number of studies the quantum confinement effect is considered to be responsible for C-Dots PL properties in a similar behavior with the "classic" semiconductor Quantum Dots while other opinions tend to emphasize the role of surface functional groups in achieving the excited states responsible for the excitation wavelength - dependent photo emission. The search for an accurate description of the PL mechanism is further complicated by a significant number of studies which report up-conversion luminescence, usually from NIR (800-850 nm) to the blue-green area of the visible spectrum. Whilst, the observed up-conversion PL of the C-Dots is still controversial this feature, if widely confirmed, may be highly regarded for the bio-imaging applications or by the attempts of further increasing the efficiency of solar energy conversion systems.

The process which undergoes during pyrolysis of NHS leading to C-Dots is summarized in Figure 1(a). Figure 1(b,c) presents the visually tested emission of the prepared C-Dots dispersed in water under excitation with a UVA laboratory lamp (b) and a 440 nm laser (c). As could be noted,

the excitation-dependent emission is clearly highlighted, the PL emission being shifted from blue to green. Chromaticity parameters according to CIE 1931 color space recorded at 360 nm and 420 nm excitation wavelengths are included in supporting information, Figure 2.

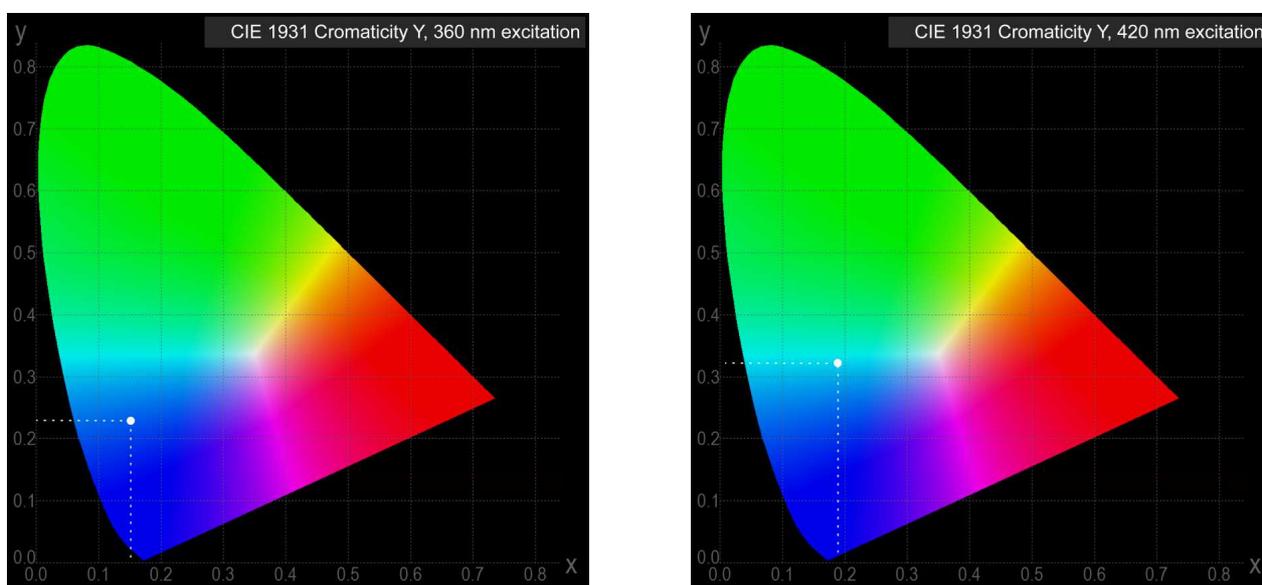
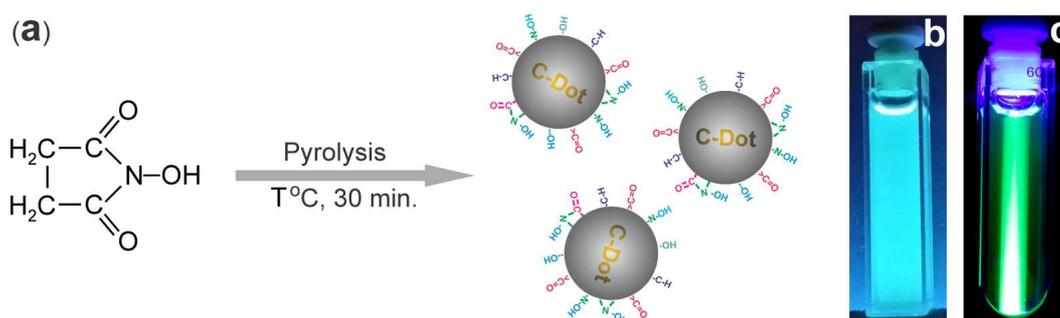


Figure 2. Chromaticity parameters according to CIE 1931 color space recorded for C-Dots dispersed in acetone at 360 (left) and 420 (right) nm excitation wavelengths

The overall O, N, C concentrations as resulted from the XPS survey spectrum is presented in Table 1. Figure 3 shows the recorded Raman spectrum of the prepared C-Dots. The peaks centered at 1365 and 1565 cm^{-1} are typical signatures for graphitic nanostructures, being in close accordance with other works. The slight displacements of these peaks in various reported works is due to the laser parameters used for the Raman excitation in a specific measurement setup.

Table 1. Overall C, N, O concentrations recorded for the prepared C-Dots

Element	O	N	C
Atomic concentration (%)	26.44	14.12	59.44
Mass concentration (%)	31.70	14.82	53.48

The 1565 cm^{-1} peak (G band) correspond to the in-plane stretching vibration E_{2g} mode of graphite, being related to sp^2 bonded carbon atoms while the 1365 cm^{-1} (D band) originates from the swinging bonds vibrations of carbon atoms located in the edge plane of disordered graphite, being

often referred as the disorder or defect band. The intensity ratio between the D and G bands (I_D/I_G) is proportional with the disorder degree/presence of the structural defects and also indicates the ratio of sp^3/sp^2 carbon. The prepared C-Dots present an over-unity I_D/I_G ratio suggesting the intercalation of nitrogen atoms in the carbonaceous core and/or the presence of surface located edge functional groups leading to a somehow disordered structure. The assumed functional groups rich structure of the prepared C-Dots is consistent with the results provided by FT-IR analysis (Figure 4). A multitude of peaks related to various functional groups are present in the recorded IR spectrum (see imprinted table in Figure 4).

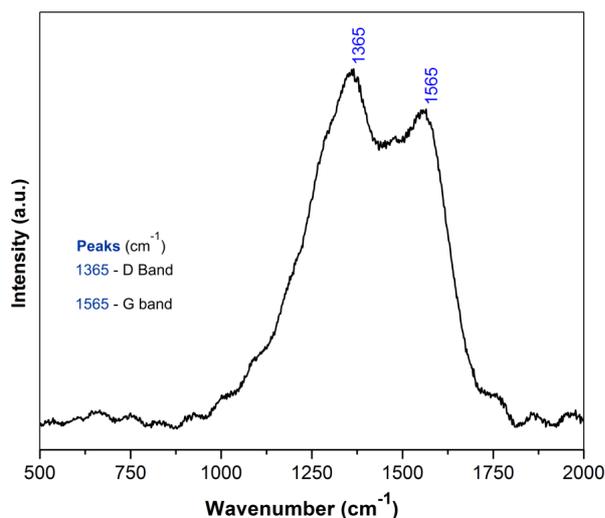


Figure 3. Recorded Raman spectrum

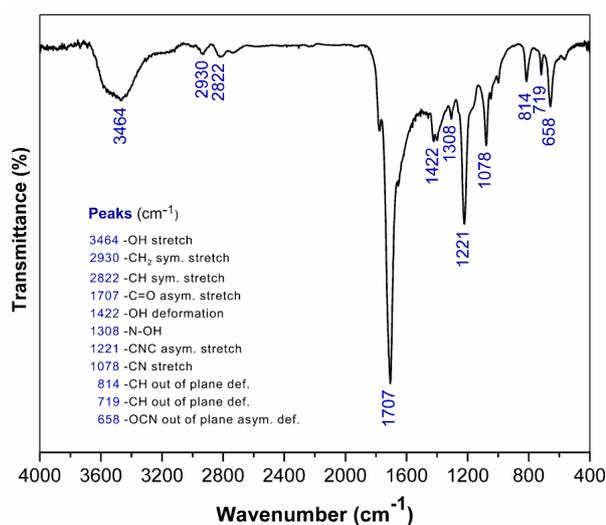


Figure 4. Recorded FT-IR spectrum including functional groups assignment

HR-TEM investigations were performed on samples prepared by drop spreading high diluted C-dots in EtOH on carbon coated, 300 mesh copper grids. Figure 5(a) reveal aggregates in 50 – 200 nm range due to the ante mentioned particles agglomeration tendency, also highlighted by AFM investigation.

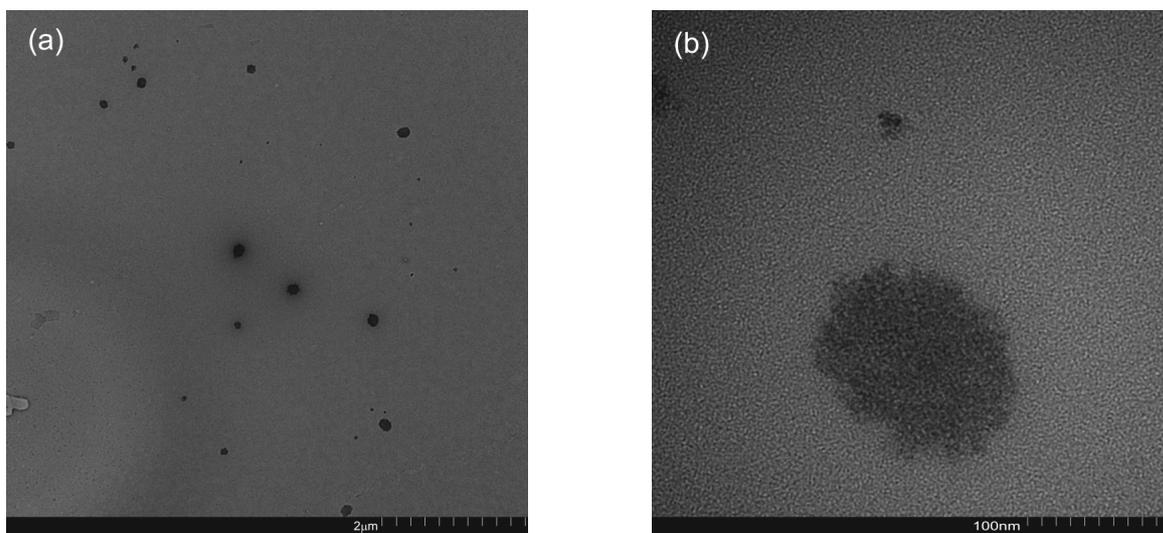


Figure 5. HR-TEM images recorded at (a) 35k and (b) 700k magnifications

A significant insight regarding the fine structuring of the aggregates were highlighted by the micrographs recorded at higher magnifications, Figure 7(b). As could be noted, the ~ 120 nm aggregate is granular in appearance, which indicates the presence of very small C-Dots in 2-5 nm range.

Luminescence properties of C-Dots are rather a result of the radiative transitions occurring within or between the functional groups located on the C-Dots surface and seem to be less dependent on their size. Recent studies emphasize the role of functional groups such as carbonyl, carboxyl and nitrogen containing groups in PL properties of C-Dots and the possibility to alter the PL emission through modification of these surface localized groups. The surface located functional groups may be responsible for various trapping states, each with different energy level, leading to an excitation dependent emission.

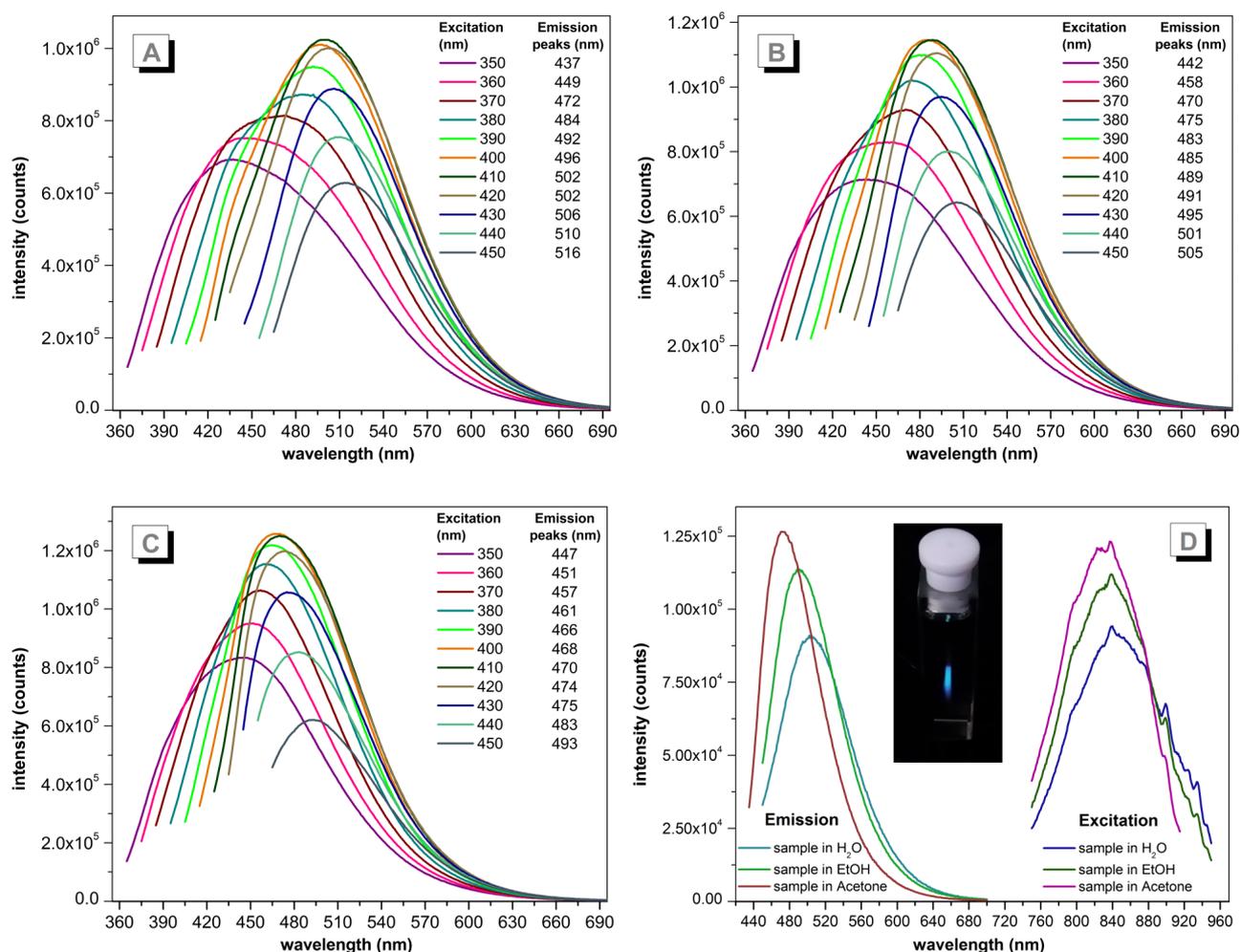


Figure 6. PL emission recorded for excitation wavelengths from 350 to 450 nm in 10 nm increments of the prepared C-Dots dispersed in (a) water, (b) EtOH, (c) acetone and (d) up-conversion emission recorded for the same samples

The dimensional characteristics of C-Dots may be important to a certain extent in achieving the PL properties but we suspect an indirect relation between them. In various works related to C-

Dots, similar PL properties were reported in case of <10 nm C-Dots but, also for those in the 10-50 nm range. One possible assumption is that a noticeable PL is achieved between certain dimensional limits. Beyond the upper limit, an oversized carbonaceous core may be less decorated with surface localized functional groups or these groups are less packed to achieve the type of interactions responsible for triggering the PL emission. The PL mechanism relying on functional groups attached on the surface of the C-Dots may provide an additionally insight on observed excitation wavelength dependence of the emission peaks. While in certain studies this dependence is explained by the concomitant presence of various dimensional species, each of them responsible by a particular emission peak, the functional group based PL can explain it by the excited states achieved within or between various functional groups, each responsible for a particular emission peak. The recorded up-conversion PL is not excitation wavelength dependent (Figure 6d) but, the PL emission peaks are different in each solvent medium (471 nm in acetone, 489 nm in EtOH and 502 nm in H₂O), in all cases the excitation peaks being recorded at 838-840 nm. Also, as in case of down-conversion fluorescence, the PL intensity is influenced in the same way by the polarity of the solvent.

To obtain electroluminescent composite were addressed two distinct directions. in first case was intended to produce a composite system implemented in electroluminescent LEC monolayer type (light emitting capacitor), in the second case of a multilayer configurations "Classical" PLED. For LEC system is in principle sufficient to produce a composite prepared by placing the luminescent nanostructures in the polymer matrix and their deposit thin films on substrates of glass/ITO-coated PET, followed by realization of the second electrode by vacuum deposition of a thin layer of Au or Al. Electroluminescent is obtained by recombination of charge carriers and stimulating corresponding excited states responsible for radiative transitions of luminescent material.

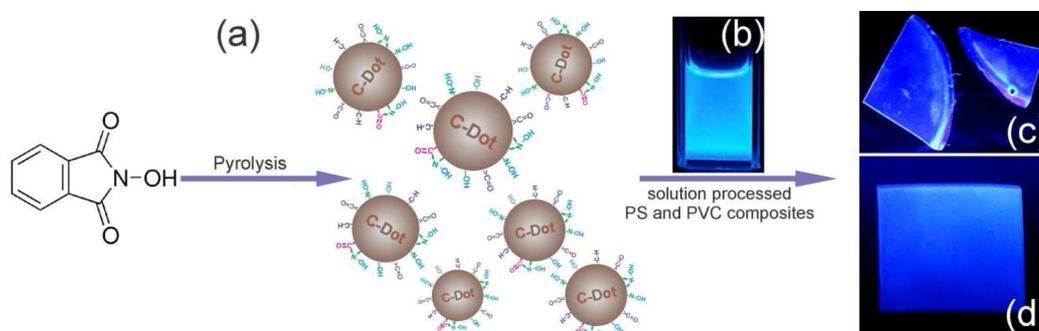


Figure 7. (a) pyrolysis scheme leading to C-Dots, (b) chloroform dispersed

C-Dots and resulted composites in (c) PS matrix, (d) PVC matrix, under excitation

Performance is directly dependent emission quantum yields of the material luminescent and to a large extent influenced by the efficiency of energy transfer to it. on

Besides the structural characteristics of the composite, electroluminescent system performance are dependent and thickness / consistency layer composite thin films deposited on the substrate. Figure 7 illustrates the principle of obtaining luminescent polymer composites for the implementation in a LEC electroluminescent system.

The average particle size of the C-Dots embedded in polymer matrix is located in 18-30 nm range but, higher dimensions (50-90 nm) being also recorded, most probable due to the agglomeration tendency. The AFM investigation (Figure 8 a,b) of the prepared composites processed in thin films on glass substrates. The size distribution of C-Dots is preserved after preparation of PS composite.

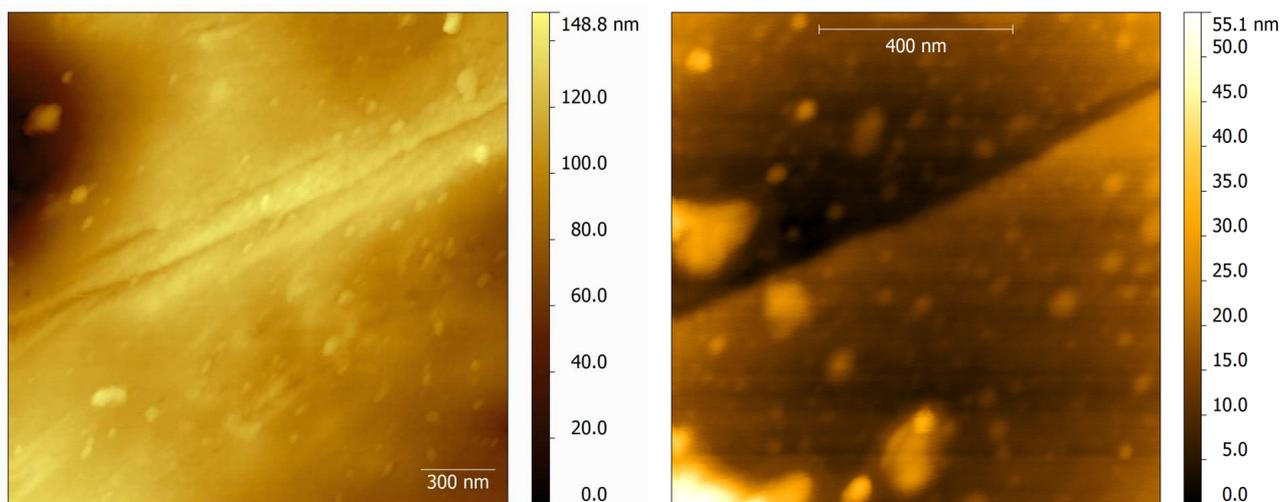


Figure 9. Recorded AFM images (a) PVC-C-Dots composite (b) PS-C-Dots composite

Figure 6 (a,b) presents the projected 3D AFM images recorded for the prepared thin PS and PVC – C-Dots composite films.

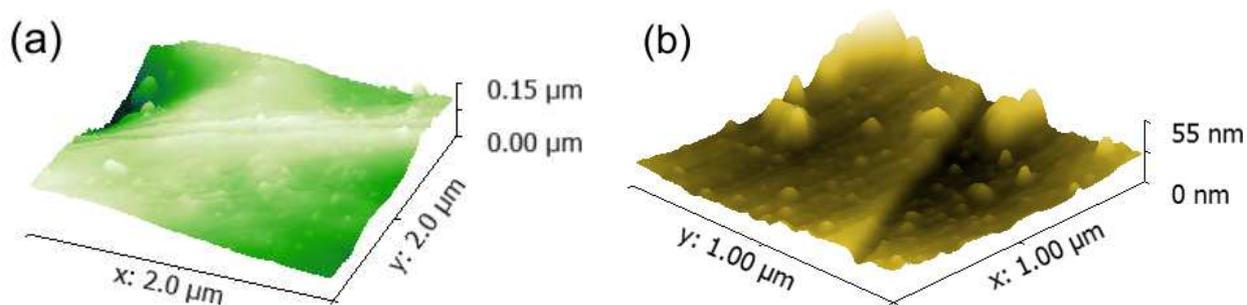


Figure 10. Projected 3D AFM images recorded for spin coated (a) PVC-C-Dots and (b) PS-C-Dots composites on glass substrates

In Figure 11 are presented the emission spectra recorded at different excitation wavelengths for the prepared C-Dots dispersed in chloroform (Fig.11a) and THF (Fig.11b) prior to embedment in the polymer matrices. As could be noted, the emission peaks were recorded within 402-472 nm range being both excitation wavelength and solvent dependent.

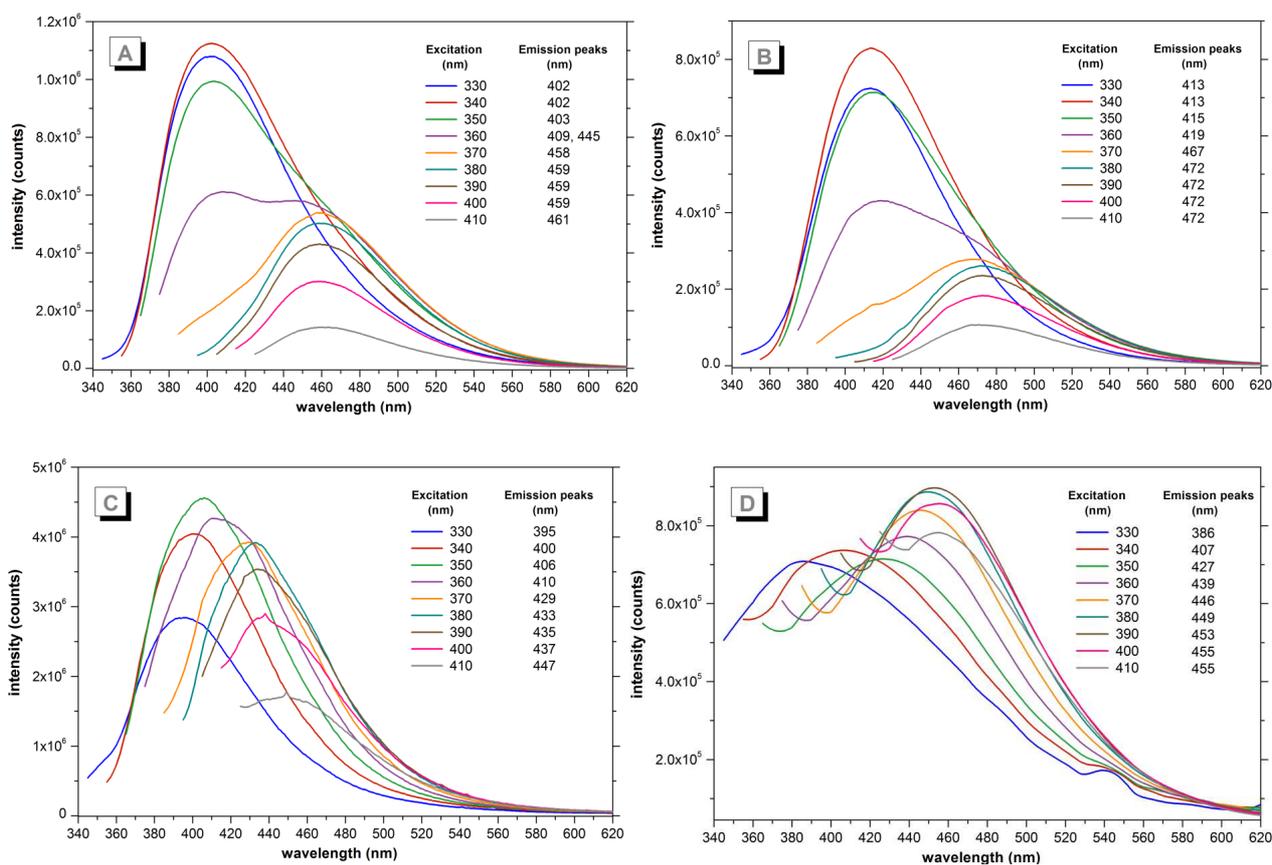


Figure 11. PL emission recorded for excitation wavelengths from 330 to 410 nm in 10 nm increments of the prepared C-Dots dispersed in (a) chloroform, (b) THF and for the (c) PS (d) PVC composites

The Stokes shifts are also solvent dependent. In case of chloroform dispersed C-Dots the emission peaks are located in 402-461 nm range (Figure 7a) while in case of THF dispersed C-Dots (Figure 7b) larger Stokes shifts were noted (413-472 nm) in this case lower energy photons being produced during the radiative processes. The recorded results from steady state fluorescence are in agreement with the absolute PLQY measurements, where the highest QY (79.95%) was recorded in case of chloroform dispersed C-Dots, the value being almost double compared to THF dispersed C-Dots (44.55%). Table 2 presents the absolute PLQY values recorded at different excitation wavelengths.

Table 2. Absolute PLQY of the C-Dots dispersed in THF and chloroform

Sample/ solvent	absolute PLQY (%)								
	excitation wavelength (nm)								
	330	340	350	360	370	380	390	400	410
C-Dots /THF	35.34	43.66	38.59	37.12	34.64	42.18	44.55	37.54	22.68
C-Dots /chloroform	34.28	43.65	49.62	51.76	56.22	60.23	79.95	69.89	47.82

The steady state fluorescence investigation of the polymer composites processed in thin films or monoliths (Figure 11 c,d) revealed same excellent emission properties due to the proper preservation of the embedded C-Dots PL properties. Obviously, the emission intensity is proportional with the concentration of C-Dots in the polymer matrix which is limited only by their agglomeration tendency which tend to reduce the overall emission intensity and the consistence of

the composites. Certain changes in the recorded emission spectra were recorded, the most notable being the Stokes shifts which in both prepared composites are smaller compared with the free C-Dots dispersed in chloroform or THF. The peak emission range is shifted to smaller wavelengths (385-447 nm for PS and 386-455 nm for PVC composites), higher energy photons being produced in the radiative processes due to a more efficient energy transfer to the excited states. In solution, non-radiative deactivation paths are more efficient due to the vicinity of solvent molecules, while in case of solid composites these processes are minimized.

Simultaneously, in 2014 research stage were continued experimental activities for the optimization of the multilayer structure of the electroluminescent cell on the basis of CdSe QD prepared in the previous steps. After testing, it was revealed the need for a configuration consisting of 4 layers successively deposited onto the glass / ITO as follows: 1. PEDOT-PSS; 2. PSSA-PANI composite layer; 3. CdSe nanocrystals layer; 4. electron injection layer made of LiF. Also were tested a number of other compounds acting as electron transport or hole like bathofenanthroline and 2- (1H-1,2,4-triazol-3-yl) pyridine, the results of these additions in supplemental layers being inconclusive. The first 3 layers were deposited by spin coating. In case of the LiF, the only option was to use art PLD (pulsed laser deposition). The experimental study was carried out using PLD equipment from ICMPP Petru Poni Iasi. The second electrode was obtained by vacuum deposition of a gold layer with a thickness of approx. 80 nm.